# Preparation and Superconductivity of Multilayered V/Ag Films with Artificial Superstructure (Commemoration Issue Dedicated to Professor Toshio TAKADA On the Occasion of His Retirement)



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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 64, No. 4, 1986

# Preparation and Superconductivity of Multilayered V/Ag Films with Artificial Superstructure

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*Received June 10, 1986*

Multilayered V/Ag films with artificial superstructures were successfully prepared by alternate deposition of two elements in UHV. The X-ray diffraction profiles changed with the film composition. Calculations were carried out based on a simple structural model to elucidate the film structure. Preliminary measurements on the superconductivity indicated that the films were a useful model system for the study of proximity-coupled multilayered superconductors.

KEY WORDS: X-ray diffraction/ Superconductivity/ Multilayered film/ V/Ag

## I. INTRODUCTION

Recently multilayered systems with artificial periodicity draw much attention. Multilayered films which consist of metal elements are now widely investigated as well as well-known examples of semiconductor superlattices. Synthesis of the metallic multilayered films with artificial periodicity has two major purposes. One is to make model systems for fundamental science and the other is to make new materials which do not exist in nature.

We have studied magnetic multilayered systems such as Fe/Sb[1], Fe/V[2] and Fe/Mg[3]. To develop the study on the multilayered systems we intended to make superconducting multilayered films. V metal was chosen as a superconducting element and Ag metal as a normal metal element. V metal is an intrinsic type II superconductor with the transition temperature of 5.4 K. The combination of V and Ag was selected because they were not miscible in solid and even in liquid states and alloy formation at the V/Ag interface should be negligible. Several studies were reported about the superconducting multilayered films containing Nb as a superconducting element[4,5], but few systematical studies were done for other elements within our knowledge. In the metal-superconductor combination the important interaction is a proximity effect. Multilayered V/Ag films are regarded as proximity-coupled multilayered superconductors.

As a first step to study multilayered superconducting films we investigated the possibilities to make multilayered V/Ag films with artificial periodic structure and to utilize them as a model system. The structures of the films were examined by

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X-ray diffraction. Superconducting properties of the films are briefly reported.

## II. SAMPLE PREPARATION

The multilayered films were prepared by ultrahigh vacuum (UHV) deposition method. The deposition system was evacuated down to $10^{-10}$ Torr range by a cryopump and kept $10^{-9}$ Torr range during the deposition. Two electron beam guns (E-gun) were used as heating devices. As evaporation sources, V metal flakes of 99.9% purity were directly put in a water cooled crucible of an E-gun and an Ag metal ingot of 99.9% purity was put on a Ta dish which was set in a crucible of another E-gun to reduce heat dissipation. A liquid $N_2$ trap was located around the heating devices in order to diminish out gases. The sources were alternately deposited onto a mylar and/or a polyimide sheet and glass substrates with the rate of 0.3 Å/s. A programmable quartz thickness monitor was used to measure film thicknesses. A sensor head was placed near the substrate. To calculate film thicknesses only a geometrical factor was corrected and the other parameters were assumed to be the same as the bulk values. The programmable thickness monitor actuates two shutters situated just above the evaporation sources at preset points to control film thicknesses. Other two sensor heads near the E-guns monitor each evaporation rate of the sources irrespective of shutter motion. Substrate temperature was chosen to be room temperature to obtain better adhesion of the films to the substrates[6]. The substrates were not cooled but the temperature increase during the deposition was negligible.

Table I. Nominal structure and superconducting transition temperature of multilayered films.

| sample no. | thickness of V (Å) | thickness of Ag (Å) | number of bilayers | $T_c$ (K) |
|---|---|---|---|---|
| #1 | 10 | 100 | 55 | — |
| #2 | 15 | 30 | 30 | 1.3 |
| #3 | 20 | 20 | 50 | 1.6 |
| #4 | 20 | 40 | 50 | 1.4 |
| #5 | 30 | 15 | 40 | 2.4 |
| #6 | 40 | 20 | 30 | 2.9 |
| #7 | 100 | 50 | 20 | 3.7 |
| #8 | 100 | 100 | 15 | 3.5 |
| #9 | 100 | 200 | 15 | 2.7 |
| #10 | 150 | 50 | 10 | 4.2 |
| #11 | 160 | 320 | 10 | 2.9 |
| #12 | 200 | 400 | 10 | 3.5 |
| #13 | 240 | 480 | 7 | 3.4 |

The structures of the prepared films are listed in Table I. The first and the last layers of each film are Ag layers of more than 100 Å thickness for buffer and protection. The samples #7, #8 and #9 were prepared for the purpose to study about the behavior of the field penetration into Ag layers in the superconducting state and the samples #11, #12 and #13 to observe dimensional crossover in the temperature dependence of upper critical field. The samples with V layers thinner than 40 Å were mainly for structural study.

## III. EXPERIMENTAL

The structures of the multilayered films were investigated by X-ray diffraction with keeping scattering vector parallel or perpendicular to the film plane. A conventional powder diffractometer with Cu K$\alpha$ radiation was used and no modification was done in case of parallel scan. The films on glass substrates were used for perpendicular scan and the films on polyimide sheets were used for parallel scan to get enough X-ray transmission. As a mylar sheet gave a peak around V (110) in the parallel scan, it was unsuitable for X-ray measurements in the present case.

Superconducting transition of the multilayered films was measured by dc electrical resistance and inductive change. For the resistance measurement, the films on mylar sheets were cut into rectangular shape (1 mm$\times$10 mm), and the conventional four prove method was adopted. Inductive transition was observed by the use of Hartshorn-type mutual inductance bridge, where ac magnetic field (1.7–500 mOe) was applied perpendicular to the film plane cut in 7 mm $\phi$ disk.

## IV. RESULTS AND DISCUSSION

Small angle X-ray diffraction measurements were carried out to confirm the formation of the artificial periodicity along the direction of the film growth with

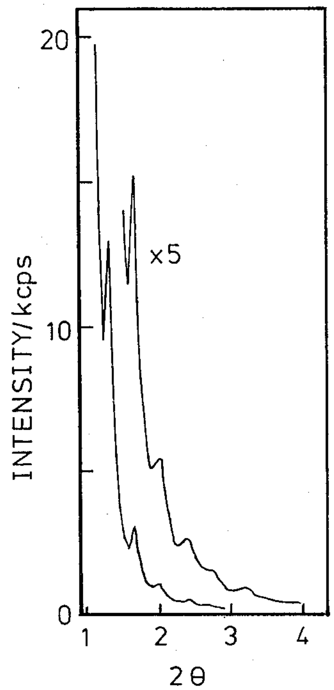


Fig. 1. A typical X-ray diffraction profile of the multilayered film in small angle region. The observed peaks are Bragg reflections corresponding to the artificial periodicity.

keeping the scattering vector perpendicular to the film plane. Several Bragg peaks corresponding to the artificial periodic length were observed for all samples whose bilayer thicknesses were shorter than 300 Å and thus the films were directly proved to have periodic structures. A typical X-ray diffraction pattern is shown in Fig. 1. It is expected that the modulation mode of the periodic structure is nearly square wave because many higher order peaks are detected. In the samples with longer periods no Bragg peak due to the artificial periodicity was observed because the peak spacings were too close to be resolved. However, judging from the results for the samples with shorter periods, it is expected that the periodic structures were also established in the samples with longer periods.

The length of the artificial period was calculated from the observed peak positions with using Bragg formula and compared with a sum of the thicknesses for single V and Ag layers. As shown in Fig. 2, both values coincide with each other.

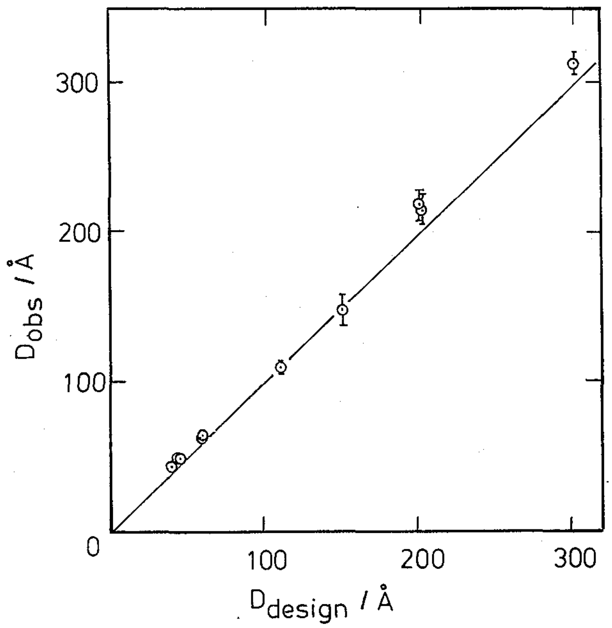


Fig. 2. Comparison of the observed periodic length ($D_{obs}$) with the designed one ($D_{design}$).

This shows that the film thickness measured by the thickness monitor is fairly reliable. It was concluded from the small angle X-ray diffraction that the designed superstructures were well established in the prepared films.

The stacking structure of V and Ag layers was examined by scanning the higher angle range. First we discuss about the samples whose periods are shorter than 100 Å. Several peaks were observed around the calculated peak positions for bcc V (110) and fcc Ag(111) and no appreciable peaks were detected in the other region. This suggests that V(110) and Ag(111) planes are preferentially oriented parallel to the film plane. The X-ray diffraction patterns for different film compositions are reproduced in Fig. 3. The patterns are not a simple sum of V and Ag peaks

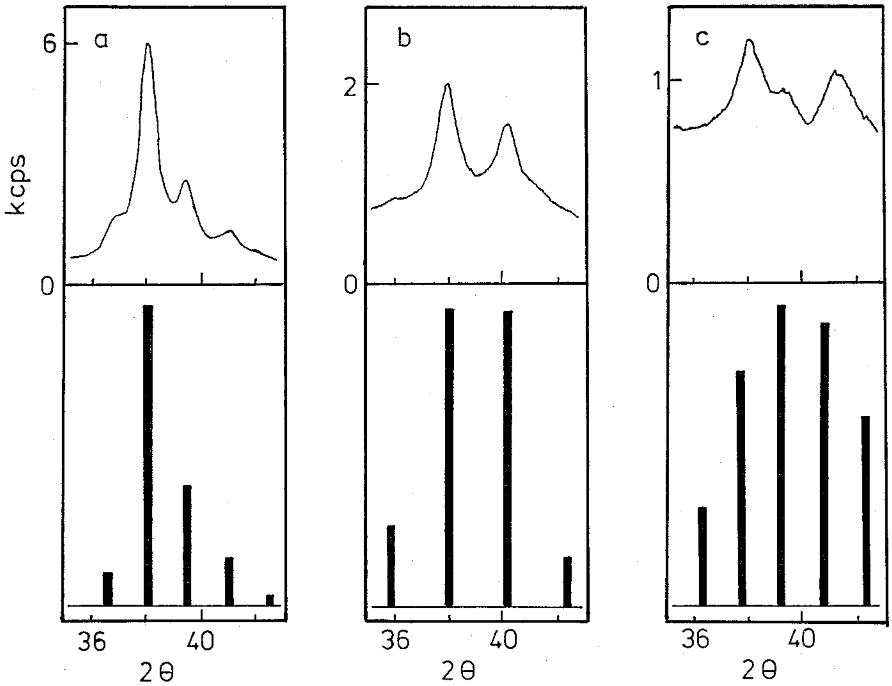


Fig. 3. X-ray diffraction patterns for different film compositions. a) sample #4, b) sample #3, c) sample #6. Calculated profiles based on a structural model are shown in the lower part.

but consist of several ripples because the artificial periodicity introduces new reciprocal lattice points. It was shown that the step model was a good structural model in some metallic superstructures[7~9]. Calculations were carried out based on the simple step model to explain the observed patterns. In the model following things were assumed: 1) V(110) and Ag(111) planes are coherently stacked along the direction of the film growth. 2) Composition modulation is a square wave. 3) V and Ag layers maintain their bulk structures. 4) Interface plane spacing is an average of V and Ag layer spacings. Calculated peak positions and intensities are shown in the lower part of Fig. 3. Though this model is very simple, it simulates the observed pattern of sample #4 rather well. This model can be applied to sample #3 though the fitting becomes worse, but it cannot be applied to sample #6. Some parameters were adjusted in the framework of the simple step model to simulate the pattern of sample #6. The peak positions could be reproduced but no reasonable agreement was obtained in the intensities.

It is found from Fig. 3 that the peak width is broader and X-ray reflectivity is lower when the film composition becomes V-rich. The same tendency was seen in the samples #2 and #5. This suggests that the crystallinity of the superstructure changes systematically with the film composition. When the film composition is Ag-rich, the superstructure is described rather well by the simple step model.

But when the film composition becomes V-rich, crystal imperfection may be introduced in the superstructure and may change the diffraction profile. At the present stage no structure model can be proposed to reproduce the X-ray pattern of sample ♯6.

In the above discussion V and Ag layers were assumed to have their bulk crystal structures. However according to Brodsky, thin Cr layer sandwiched by thick Au layers (fcc) changed its structure from bcc to fcc[10]. To examine such possibility in the V/Ag combination, X-ray diffraction measurements were carried out with keeping the scattering vector parallel to the film plane, where the artificial periodicity gave no effect on the diffraction profiles. The result for sample ♯3 is shown in Fig. 4. The observed peaks could be assigned with assuming that V was bcc and Ag was fcc. No evidence was observed for fcc V.

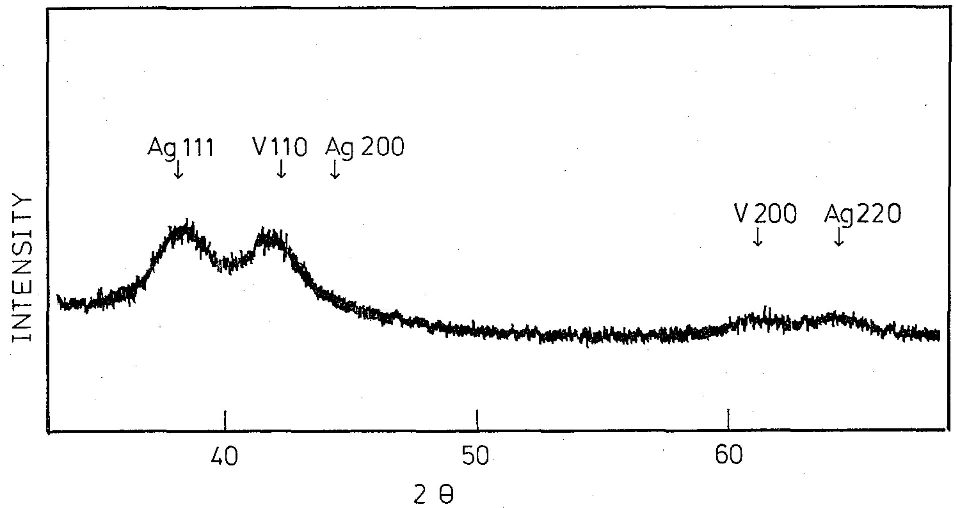


Fig. 4. The result of the X-ray diffraction for sample ♯3 with keeping the scattering vector parallel to the film plane. The arrows indicate the calculated peak positions for the bulk structures.

Concerning the samples with longer periods, all peaks which appeared in a powder case were observed in the perpendicular scan but their intensities were different from the powder case. This indicates that the preferential orientation of V(110) and Ag(111) planes which was seen in the samples with shorter periods still remained but the degree of the orientation was not very high. The stacking of V and Ag layers was considered incoherent because the peak widths depended mainly on the single V or Ag layer thickness.

Superconducting properties of the multilayered films were investigated both by means of dc electrical resistance and inductive change. Superconducting transition was observed for all samples except sample ♯1, in which no transition appeared down to the lowest temperature available, 1.3 K. A typical transition width observed in dc resistance measurements was 30 mK. In all samples, perfect diamagnetism was found in real component ($\chi'$) of inductive change after completion of transition, and imaginary component ($\chi''$) formed a single peak around the transition point. Typical results are shown in Fig. 5. It is known that $\chi''$ component is very sensitive for sample homogeneity[11]. The observed sharp transition, especially a single peak in $\chi''$, supports the uniformity of the films. It was confirmed that both resistive and inductive transitions were reproducible for heat cycles between 1.3 K and 300 K. We thus concluded that present samples had satisfactory quality for the detailed study on the superconducting properties of multilayered system.

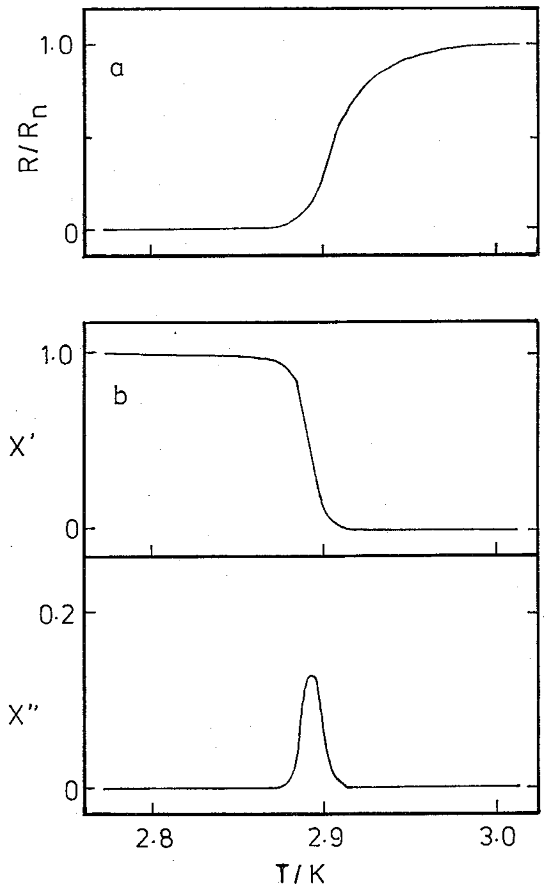


Fig. 5. Temperature dependence of a) normalized dc resistance ($R/R_n$) and b) inductive change for sample #6 near the superconducting transition point.

Superconducting transition temperatures ($T_c$) determined by dc resistance are listed in Table I. It is seen that $T_c$ becomes lower when V thickness decreases, or when Ag thickness increases. Although this tendency is qualitatively understood through the proximity effect, quantitative characterization cannot be attained because there are possible other factors to be considered (for example, dimensionality of superconductivity). We are now engaged in the study of single V films and Josephson-coupled multilayered V/Si films. We believe these data must serve for quantitative understanding of $T_c$.

Further studies on other superconducting properties of the multilayered V/Ag films are in progress. We have revealed dimensional crossover in the curves of upper critical field vs. temperature for samples #12 and #13. Particular characteristics in the curves of field penetration depth vs. bilayer period have also been found. Details are reported elsewhere[12,13].

In summary multilayered V/Ag films with artificial periodicity were successfully prepared by alternate deposition of two elements in UHV. It was shown that the films are a promising model system for the study of the proximity-coupled multilayered superconductor.

## ACKNOWLEDGEMENT

The authors would like to thank Professor Emeritus T. Takada for continued encouragement and Dr. N. Nakayama for useful discussion.

## REFERENCES

( 1 ) T. Shinjo, N. Hosoito, K. Kawaguchi, T. Takada, Y. Endoh, Y. Ajiro and J.M. Friedt, *J. Phys. Soc. Jpn.*, **52**, 3154 (1983).
( 2 ) N. Hosoito, K. Kawaguchi, T. Shinjo, T. Takada and Y. Endoh, *J. Phys. Soc. Jpn.*, **53**, 2659 (1984).
( 3 ) K. Kawaguchi, R. Yamamoto, N. Hosoito, T. Shinjo and T. Takada, *J. Phys. Soc. Jpn.*, **55**, 2375 (1986)
( 4 ) S.T. Ruggiero, T.W. Barbee, Jr. and M.R. Beasley, *Phys. Rev.*, **B26**, 4894 (1982).
( 5 ) C.S.L. Chun, G-G. Zheng, J.L. Vicent and I.K. Schuller, *Phys. Rev.*, **B29**, 4915 (1984).
( 6 ) First the deposition was made onto the cooled substrate like the previous studies (Refs. 1–3). However the cooled substrate was unsuitable in the present case. The adhesion of the film was so weak and the reproducibility in the superconducting measurements was unsatisfactory.
( 7 ) I.K. Schuller, *Phys. Rev. Lett.*, **44**, 1597 (1980).
( 8 ) Y. Endoh, K. Kawaguchi, N. Hosoito, T. Shinjo, T. Takada, Y. Fujii and T. Ohnishi, *J. Phys. Soc. Jpn.*, **53**, 3481 (1984).
( 9 ) Y. Fujii, T. Ohnishi, T. Ishihara, Y. Yamada, K. Kawaguchi, N. Nakayama and T. Shinjo, *J. Phys. Soc. Jpn.*, **55**, 251 (1986).
(10) M.B. Brodsky, *J. Magn. & Magn. Mater.*, **35**, 99 (1983).
(11) T. Ishida and H. Mazaki, *Phys. Rev.*, **B20**, 131 (1979).
(12) K. Kanoda, H. Mazaki, T. Yamada, N. Hosoito and T. Shinjo, *Phys. Rev.*, **B33**, 2052 (1986).
(13) K. Kanoda, H. Mazaki, T. Yamada, N. Hosoito and T. Shinjo, *Phys. Rev.*, **B34**, (1986) in press